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Linear and Non-Linear Electro-Optic Studies of the Smectic-A – Smectic-C_α* Phase Transition

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Electro-optical measurements have been performed around the SmA-SmC_α* phase transition point in antiferroelectric liquid crystals MHPOBC and MHPOCBC. In both materials the soft mode condensation is clearly seen in addition to the partial softening of the ferroelectric soft mode. The Curie Weiss law is observed. The comparison of the slopes of these modes shows that MHPOBC and MHPOCBC should be close to the critical point. In addition to these soft modes, a low frequency mode was detected.

Keywords: antiferroelectric liquid crystals; electro-optic effect; MHPOBC; MHPOCBC; soft mode

INTRODUCTION

The structure of SmC_α* was recently determined to be an incommensurate phase with the layer spacing [1] indicating that the soft mode should condense at a general point $\mathbf{q}_c$ of the smectic Brillouin zone. On the other hand, unusually large pretransitional fluctuations have been reported in the vicinity of the SmA–SmC_α* phase transition by heat capacity [2] and birefringence measurements [3]. Quite recently, we have shown that the pretransitional fluctuations are also observable by means of electro-optical measurements [4]. Then, we have reported

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the first observation of the soft mode in the SmC_α^* phase in MHPOCBC [5] and found that the SmA- SmC_α^* phase transition is close to the critical point.

Here we present the results of linear and non-linear electro-optic measurements of chiral tilted smectic compounds, MHPOBC and MHPOCBC, which exhibit the direct phase transition from SmA to SmC_α^*. The soft mode related to the SmA-SmC_α^* phase transition is compared in both materials and the results are discussed.

ELECTRO-OPTIC EFFECT IN THE SMECTIC-C_α^* PHASE

The variation of the light intensity ΔI under an a.c. electric field $E = E_0 \cos 2\pi ft$ to a cell between crossed polarizers can be expressed up to the second order with respect to the field as follow: [6]

$$\Delta I / I_o = 2\sin 4\alpha_o \sin^2(\beta n_{a,0})\Delta\alpha + 4\cos 4\alpha_0 \sin^2(\beta n_{a,0})\Delta\alpha^2 + \beta \sin^2 2\alpha_0 \sin(2\beta n_{a,0})\Delta n_a \quad (1)$$

where $\beta = \pi d/\lambda$, I_0 is the incident light intensity, d is the cell gap, λ is the incident wavelength, α_0 and $n_{a,0}$ are the angle of the optical axis with respect to one of the polarizer directions and the anisotropy of refractive index in the absence of the field, respectively, and $\Delta\alpha$ and Δn_a are electrically induced parts. The first term gives contribution to the first harmonic electro-optical response while the others give the contribution to the second one.

The dynamics of SmA-SmC_α^* under a.c. electric field has been theoretically studied by Bourny et al [5]. According to them, the contributions of the ferroelectric soft mode and the soft mode related to this transition can be excited by an electric field. The contribution of the ferroelectric soft mode is proportional to the field and therefore it gives the Pockels effect $\Delta\alpha$ in electro-optical responses as

$$\Delta\alpha(f) = a_f \mathrm{Re}[\chi_f(f)\, e^{i2\pi ft}]\, E_0 \quad (2a)$$

with

$$\chi_f(f) = \frac{1}{1 + i f / f_{r,f}} \text{ and } f_{r,f} = \frac{1}{2\pi\gamma}\left(a + \lambda\xi_s^2\right) \quad (2b)$$

where χ_f and $f_{r,f}$ are, respectively, the linear susceptibility and the relaxation frequency of the ferroelectric soft mode and a_f is a constant. λ is the non-linear coupling between the ferroelectric mode and the soft mode related to the transition. This coupling constant plays an important role in the dynamical properties of the SmC_α^* phase. $\xi_s = \sqrt{-\alpha/\beta}$ is the spontaneous value under no field in the SmC_α^* phase. The coefficient α is linearly dependent on the temperature, $\alpha=b_0(T-T_C)$, where T_C is the phase transition temperature into the SmC_α^* phase. The coefficient a is linearly temperature-dependent, $a=a_0(T-T_f)$, where T_f is the transition temperature to the SmC* phase without the coupling term λ. On the other hand, the amplitude the soft mode related to the SmA-SmC_α^* transition is proportional to the square of the field. The non-linear coupling λ and the dielectric anisotropy ε_a' were shown to contribute to the Kerr effect Δn_a. The Δn_a change in electro-optic measurements is expressed as

$$\Delta n_a(f) = \mathrm{Re}[\{\chi_s(2f)(a_{s1} + a_{s2}\chi_f^2(f)) + a_{f2}\chi_f^2(f)\}e^{i4\pi ft}]\, E_0^2 \qquad (3a)$$

with

$$\chi_s(f) = \frac{1}{1 + i\, f/f_{r,s}} \quad \text{and} \quad f_{r,s} = \frac{1}{2\pi\gamma}\left(\alpha + 3\beta\xi_s^2\right) \qquad (3b)$$

where χ_s and $f_{r,s}$ are, respectively, the linear susceptibility and the relaxation frequency of the soft mode. $a_{s1,2}$ and a_{f2} are coefficients depending principally on λ and ε_a'.

By using the above equations we can fully analyse the results obtained in electrooptic measurements.

EXPERIMENTAL AND RESULTS

The chiral liquid crystals studied here are as follow :

(i) 4- (1-methyl-heptyloxycarbonyl) phenyl 4'-octylbiphenyl-4-carboxylate (MHPOBC) with the phase sequence [7], SmA - (122°C) - SmC_α^* - (120.7°C) - SmC* - (119°C) -SmC_γ^* - (118.5°C) - SmC_A^*.

(ii) 4-(1-methylheptyloxycarbonyl) phenyl 4'-octylcarbonyloxybiphenyl –4-carboxylate (MHPOCBC) with the phase sequence [8], SmA-(105.5°C)-SmC_α^*-(99.5°C)-SmC_A^*.

The compounds were injected into cells of 25μm thickness (E.H.C. Co. Ltd., Tokyo) with ITO and polyimide layers. The sample alignment was improved by using a low frequency a.c. electric field around the SmA–SmC$_\alpha$* phase transition for several hours.

The experimental set-up for the electro-optical measurements was the same in our previous paper [4]. The cell was put between crossed polarizers of a polarizing microscope, and the polarizer direction was set at $\alpha_0=22.5°$ with respect to the optical axis, where only the optical axis change $\Delta\alpha$ (Pockels effect) and the birefringence change Δn_a (Kerr effect) can be detected in the first-order and in second-order responses respectively, as is readily seen from Eq. (1). The frequency dispersions were measured from 100Hz to 1MHz at stabilized temperatures by using a hot stage. Hereafter we use a complex intensity ΔI defined as $I=ae^{i\varphi}$, where a and φ are, respectively, the amplitude and the phase in each response.

In Figure 1 are shown the temperature dependencies of the amplitudes of the first-order and the second-order responses measured at 100Hz in the cooling process for both compounds. Similar behaviours are seen in both materials. In the linear response, which originates in $\Delta\alpha$, the intensity increases gradually in the SmA phase with decreasing the temperature, and then there is a small anomaly around the transition point. This anomaly was also observed in the dielectric measurement in MHPOBC [9] and in MHPOCBC [8]. From Eqs. (2) it is easily seen that the first-order response is proportional to the susceptibility of the ferroelectric soft mode and therefore the gradual increase with decreasing the temperature in the SmA phase indicates the softening of the ferroelectric soft mode. In the second-order response, on the one hand, a gradual increase is observed also in the SmA phase, which originates in the ferroelectric soft mode due to the thermal fluctuations [4]. On the other hand, in the SmC$_\alpha$* a divergence of the intensity is observed. The origin of this anomaly is not yet clarified.

The typical frequency dispersions of the first-order ΔI_{1f} and the second-order ΔI_{2f} responses in the SmC$_\alpha$* phase of MHPOBC are shown in Figure 2. In the first response, Figure 2(a), one Debye-type relaxation is involved, which is the ferroelectric soft mode as is seen from Eqs. (2), as well as in the SmA phase. The solid line represents the best fit. These measurements give us precise information about the relaxation frequencies of the ferroelectric soft mode and its temperature dependence. We use these results later when fitting the second-order response. In the second-order response (Figure 2(b)) the frequency

dispersion curve is completely different from that the first-order one. The soft mode is seen (indicated by an arrow in Figure 2(b)). The frequency dispersion curves of ΔI_{2f} were analysed in term of Eq. (3) with a good agreement (solid lines). An another contribution has been added to take into account a low frequency mode appearing in the experiment [5].

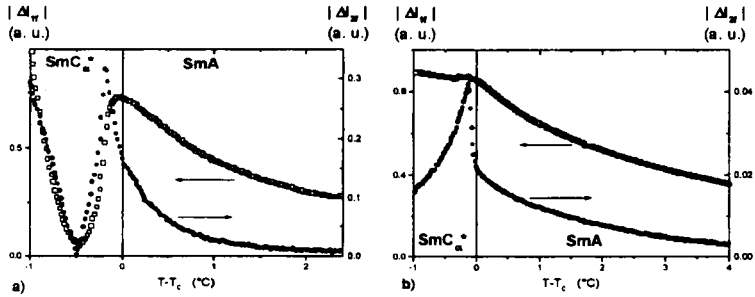

FIGURE 1 Temperature dependencies of the first-order response and the second-order one at α_0=22.5° (f=100Hz) on cooling process 0.1°C/min in **a)** MHPOBC, and **b)** MHPOCBC.

The fitting results of the relaxation frequencies of the ferroelectric soft mode $f_{r,f}$ and the soft mode $f_{r,s}$ are shown in Figures 3(a) and 3(b) for MHPOBC and MHPOCBC, respectively. In both materials, in the SmC_α^* phase the soft mode ($f_{r,s}$) related to the transition is clearly seen, and the partial softening of the ferroelectric soft mode ($f_{r,f}$) is also seen. The Curie Weiss law is observed. It should be noted that the slope of the soft mode in the SmC_α^* is about 2.7 and 3.4 times as large as the one of the ferroelectric mode in the SmA phase for MHPOBC and MHPOCBC, respectively. Assuming that in the SmA phase the slope of the soft mode, which is not experimentally obtained now, should be the same with that of the ferroelectric mode [5], the above results indicates that the SmA-SmC_α^* phase transition should be close to the critical point, as has been pointed out by Skarabot *et al* [2] and it is closer in MHPOCBC than in MHPOBC.Moreover, taking account of Eq. (2b), it is easily seen that the slopes of the ferroelectric soft mode in the SmA and the SmC_α^* phases are different due to the term $\lambda\xi_s^2$ in the SmC_α^* phase. According to the Eq. (2b) and the experimental results (see Figure 3), the non-linear coupling constant λ is positive for both compounds.

In addition to these soft modes, a low frequency mode was detected ($f_{r,l}$) in both compounds. Its relaxation frequency is almost temperature-independent and is about 500Hz and 2.5kHz for MHPOBC and MHPOCBC respectively. On the other hand, it was found, by the fitting results, that the divergence of the second-order response (see Figure 1) comes from the amplitude of this mode. The origin of this mode will be discussed elsewhere.

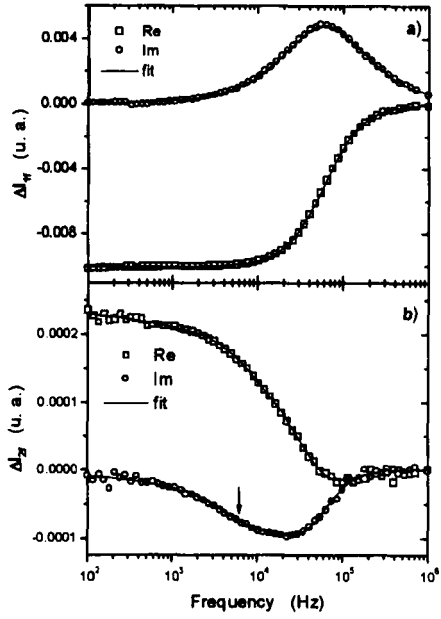

FIGURE 2 Typical frequency dispersions of **a)** the first-order response ΔI_{1f} and **b)** the second-order response ΔI_{2f} obtained at $\alpha_0 = 22.5°$ in the SmC_α^* phase of MHPOBC at $T-T_C=-0.075°C$.

In conclusion, we have shown that the second-order electro-optic response is a powerful method for observing the soft mode in the SmC_α^* phase. We have clearly observed the soft mode in the SmC_α^* indicating that the SmC_α^* phase has a simple helix and be similar to the SmC^* phase, but only different in pitch, at least near the transition point. Our results show that the six-order terms have to be included in the free energy expansion. The full analyses will be reported in future.

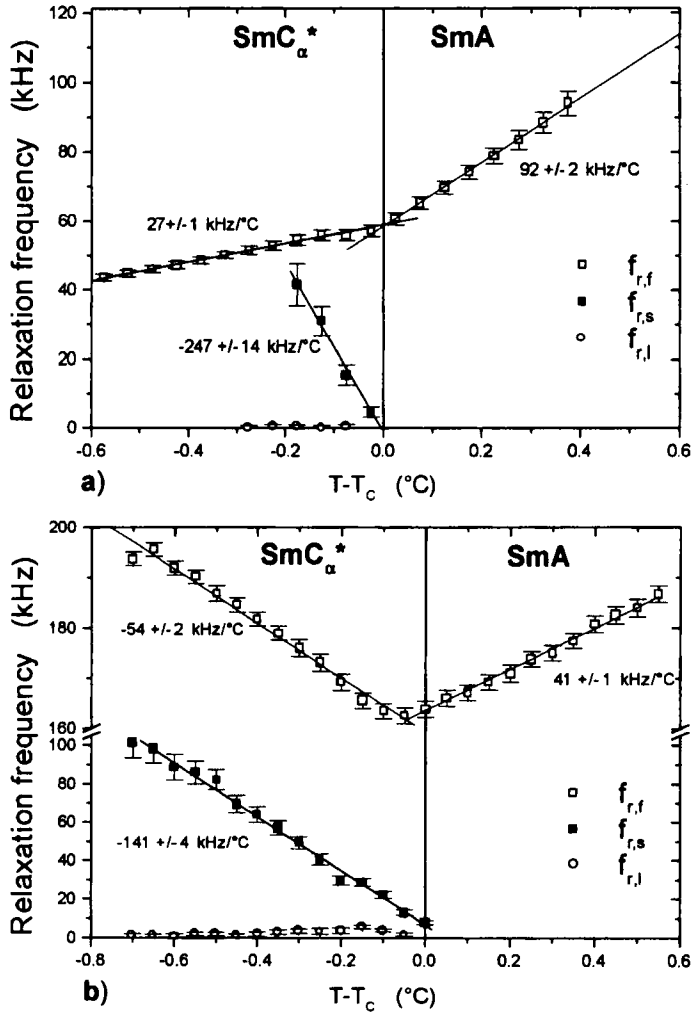

FIGURE 3 Temperature dependencies of the relaxation modes in the phase transition from SmA to SmC$_\alpha$* in **a)** MHPOBC, **b)** MHPOBC. $f_{r,f}$ and $f_{r,s}$ are the relaxation frequencies of the ferroelectric mode and the soft mode respectively, and $f_{r,l}$ is the relaxation frequency of a low frequency mode.

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